Effect of Fast Pyrolysis Conditions on Structural Transformation and Reactivity of Herbaceous Biomasses at High Temperatures

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Effect of Fast Pyrolysis Conditions on Structural Transformation and Reactivity of Herbaceous Biomasses at High Temperatures

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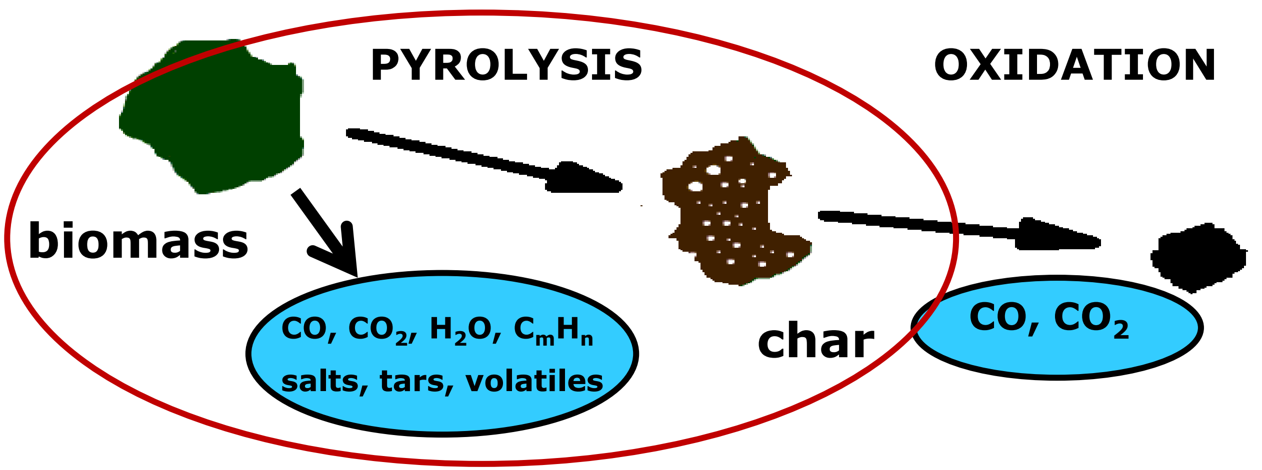
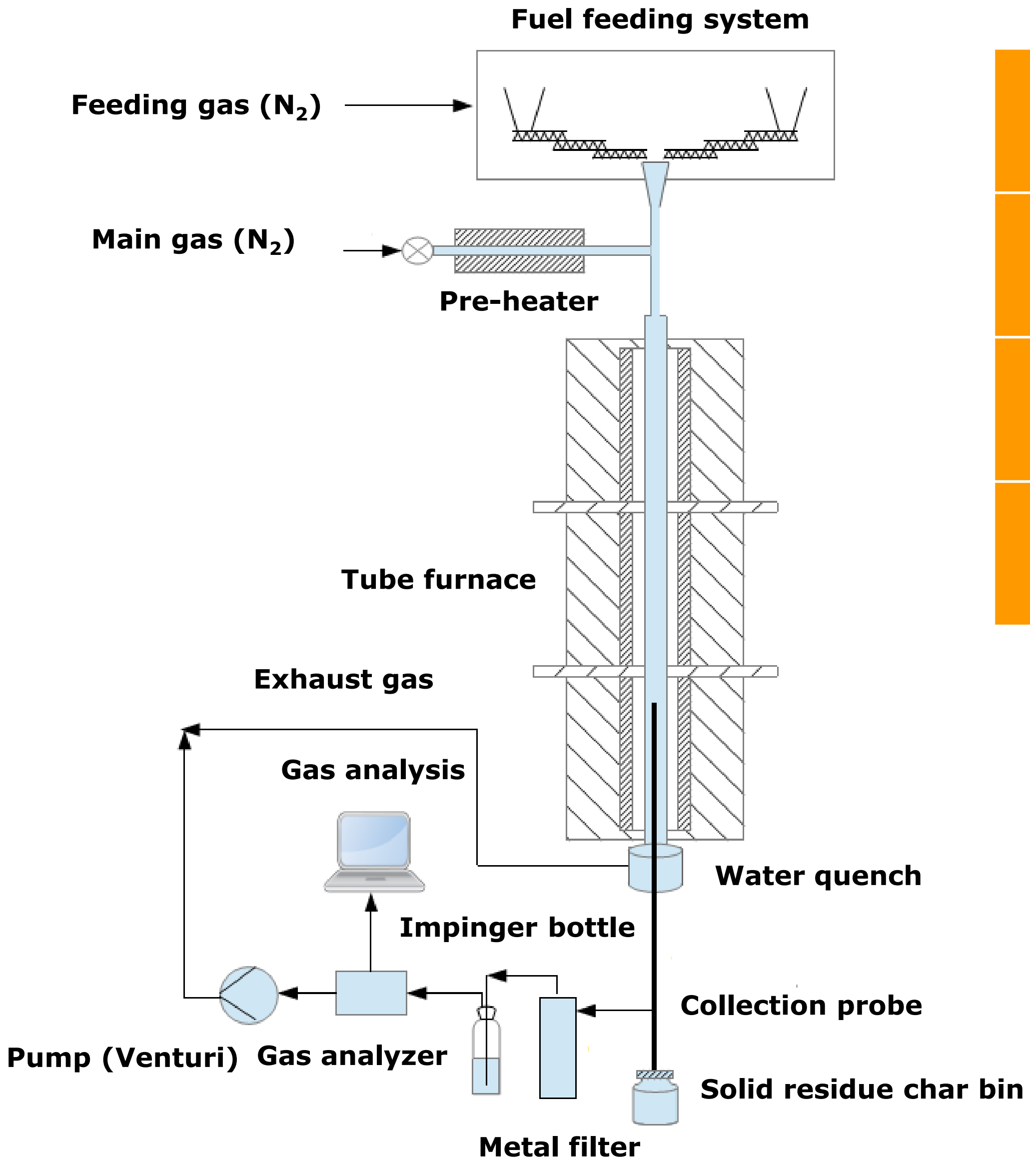
Objectives

- Herbaceous fuels (Danish wheat straw, rice husk)
- Pyrolysis of smaller particle size (0.2-0.4 mm)
- Experimental investigations at fast heating rates (10^4°C/s) and at high temperatures (up to 1500°C)
- Alkali and silicates effect on the char reactivity and morphology



TU Munich Entrained Flow Reactor (BabiTER)

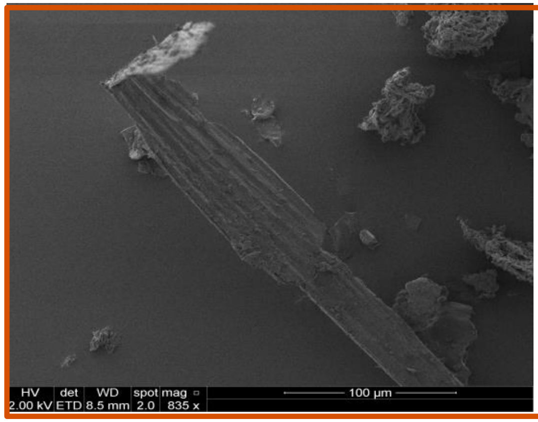


Atmosphere	N_2, O_2, H_2, CO_2,
$T_{maximal}$	1500°C
Heating rates	up to 10^4°C/s
Dimensions	L = 1.4 m D_{tube} =0.04m

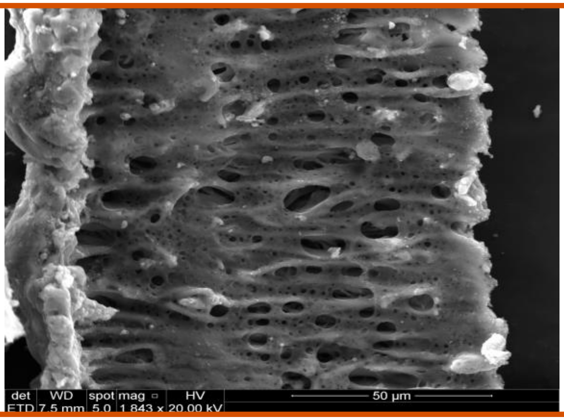
Char morphology at 1000-1500°C

Rice husk

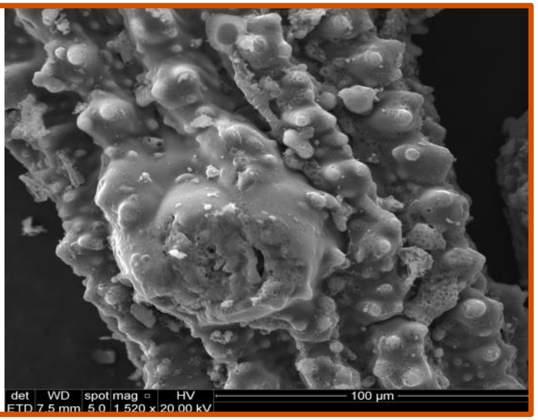
Original particles



Char inner surface, 1500°C

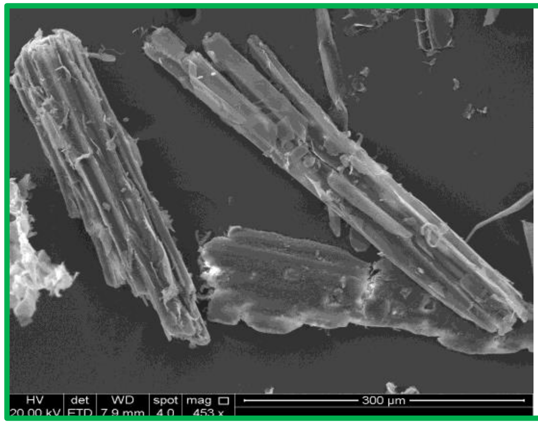


Char outer surface, 1500°C

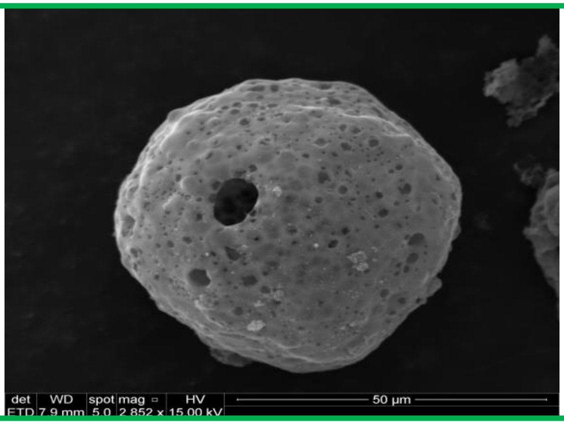


Wheat straw

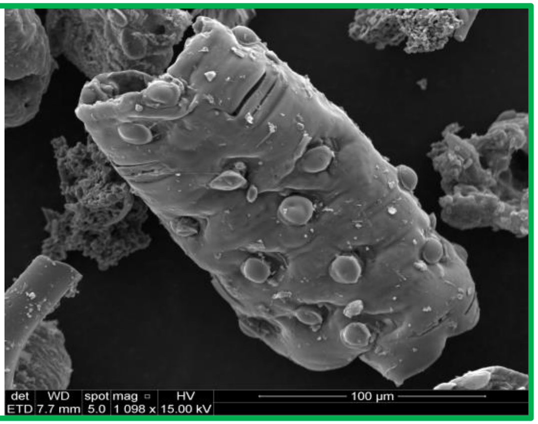
Original particles



Char, 1500°C

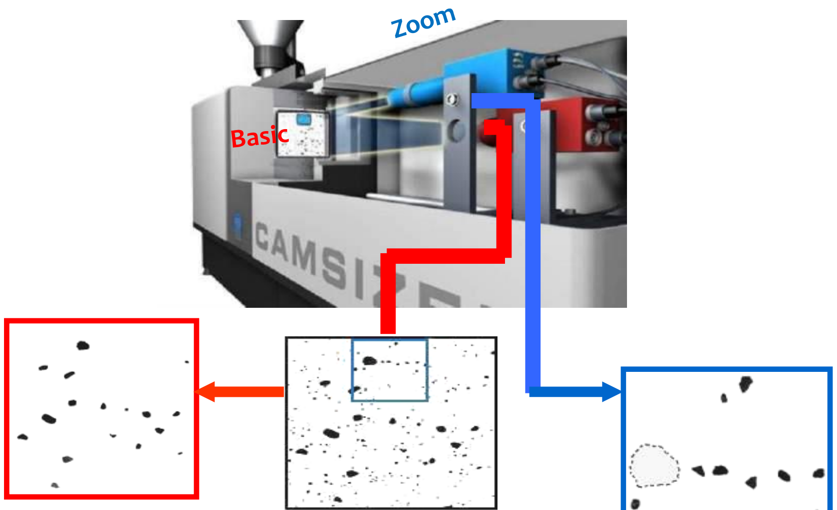


Char, 1250°C



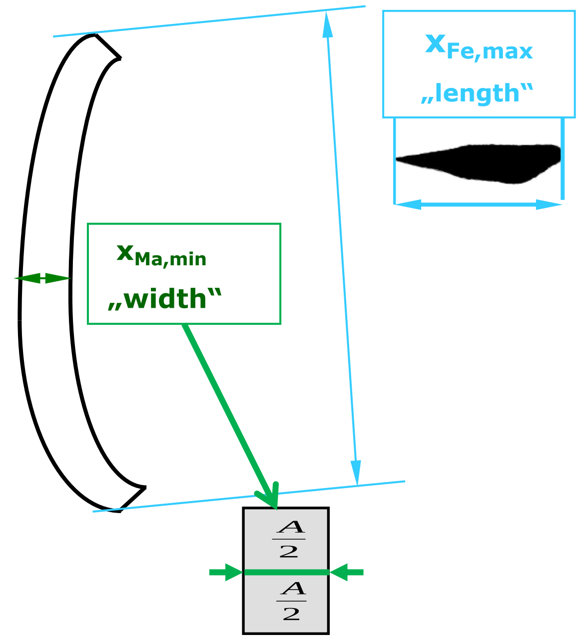
- The shape of the rice husk chars remained preserved
- Wheat straw chars obtained different shapes from near-spherical to cylindrical

Particle size analysis (CAMSIZER XT)

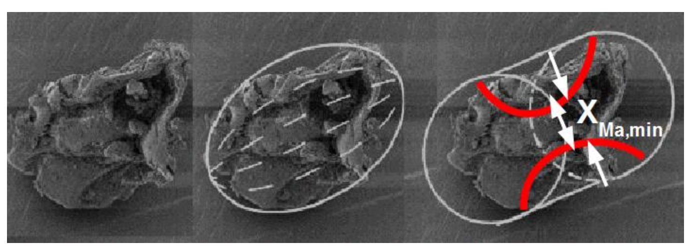


Basic-camera
(3 µm-30 mm)

Zoom-camera
(3 µm- 3mm)

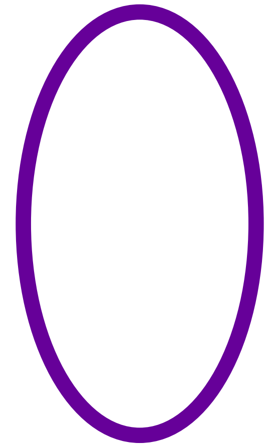


1. $\mathbf{x_{Ma,min}}$ - length of the line which bisects the particle → $$q_3 = \frac{dQ_3(X_{Ma,min})}{x(x_{Ma,min})}$$
2. $\mathbf{x_{Fe,max}}$ - distance between two maximal tangents directed parallel to each other



Particle shape analysis (CAMSIZER XT)

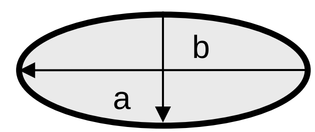
Biomass particle



Ellipsoidic representation

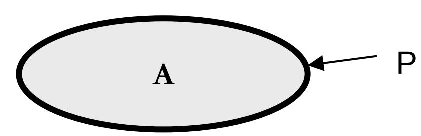
1. Ratio width ($x_{Ma,min}$) to length ($x_{Fe,max}$)

$$\frac{\boldsymbol{b}\,(\boldsymbol{width})}{\boldsymbol{l}(\boldsymbol{length})}$$



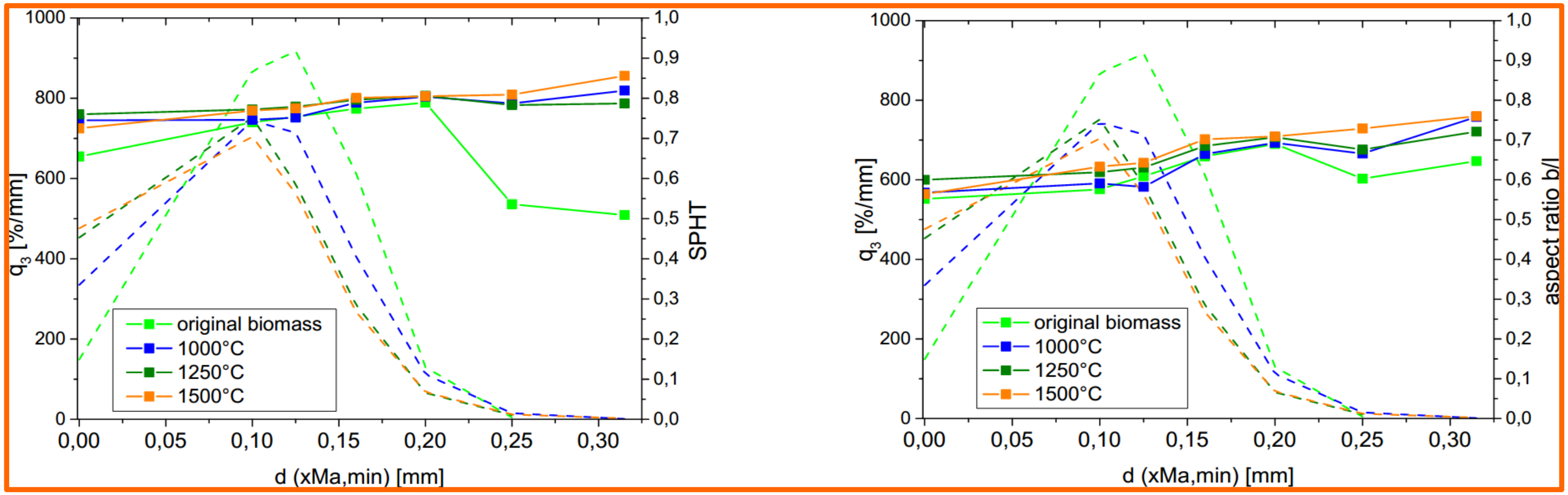
2. Sphericity (SPHT)

$$\frac{4\pi A}{P^2}$$

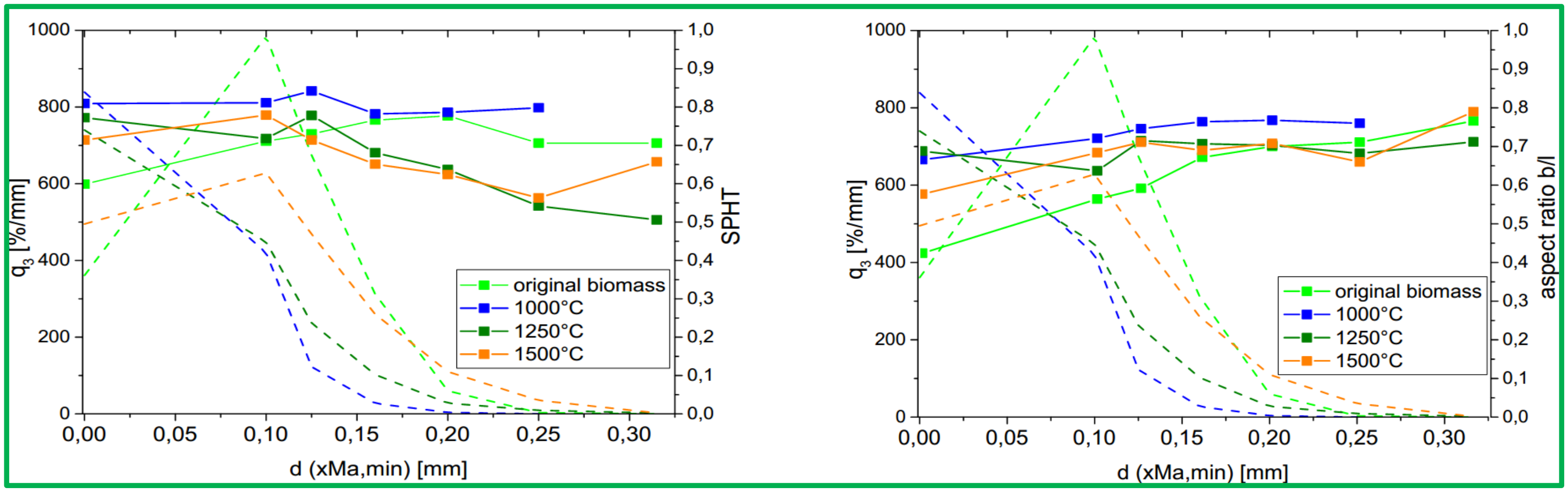


Particle size analysis

Rice husk

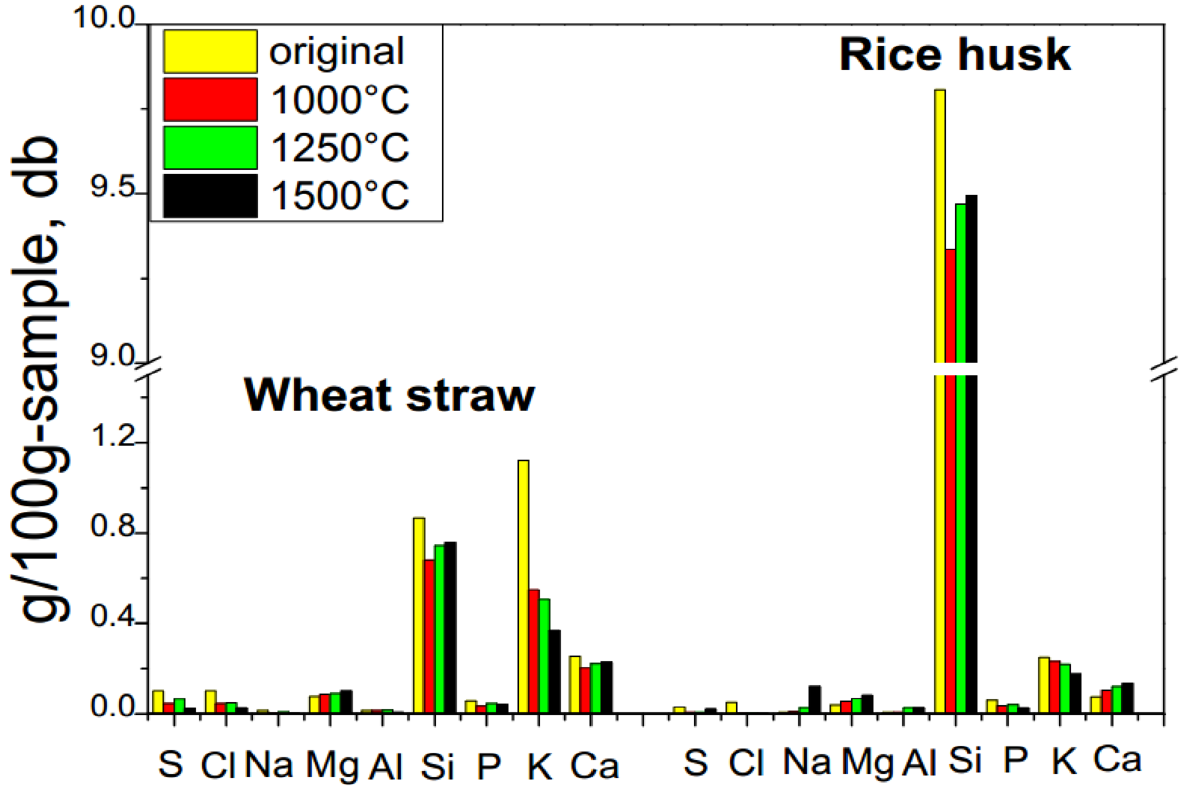


Wheat straw



- Particle size of wheat straw chars was significantly reduced compared to the raw fuel
- Rice husk char kept the particle size of the original fuel

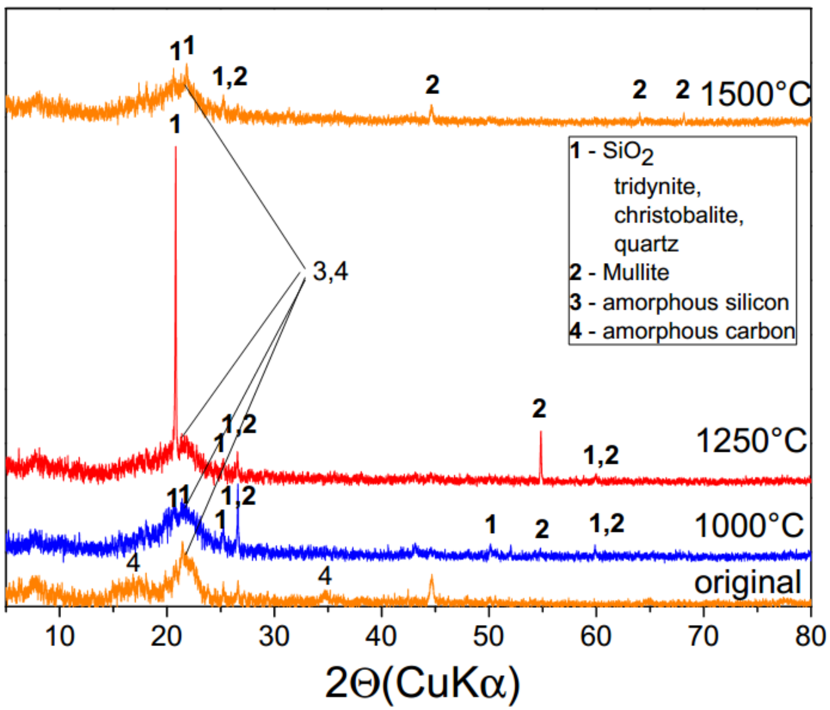
Ash compositional differences



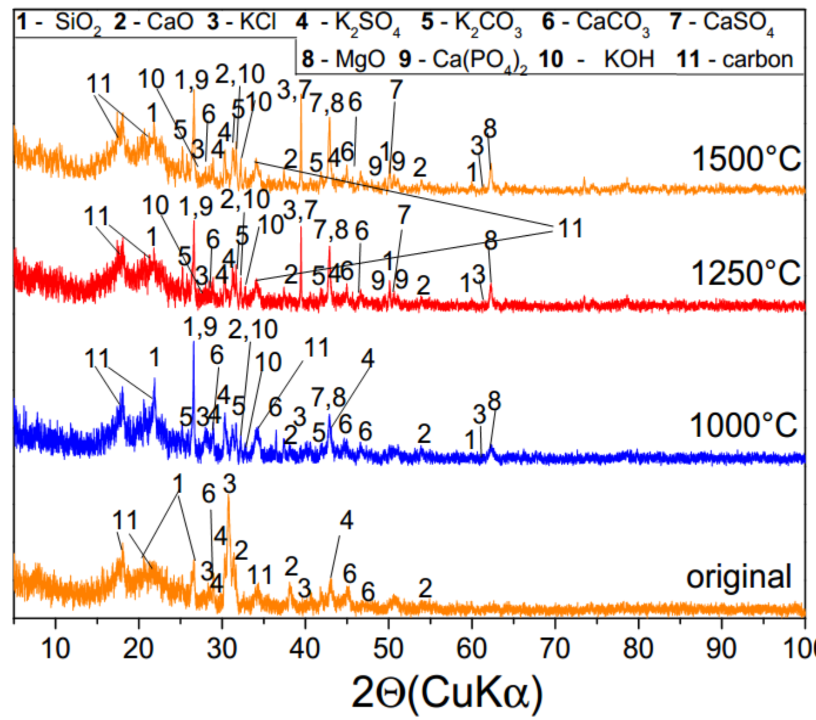
- The rice husk chars showed a high concentration of silicon oxides (> 90 wt.%) along with smaller amounts of potassium, aluminium, iron, sodium and magnesium
- The wheat straw chars contained potassium and calcium along with a high concentration of silicon

XRD analysis

Rice husk



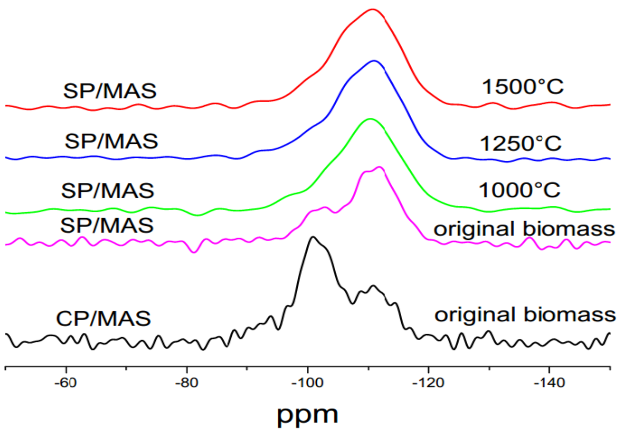
Wheat straw



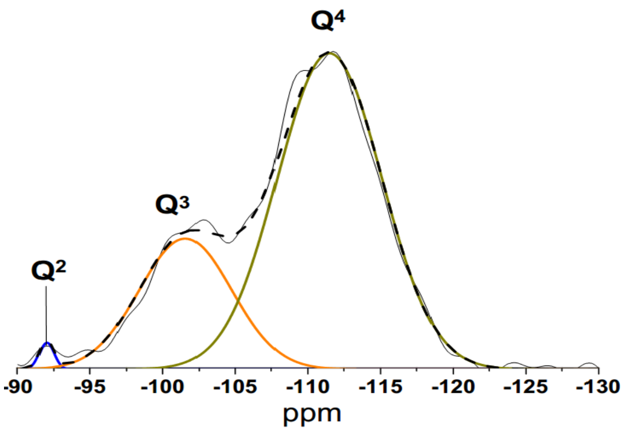
- The weak sharp and narrow reflections from crystalline silicon oxides as compared to the broad band of amorphous silicon oxides (2Θ= 21.8°) may indicate only partial crystallization under fast heating
- The XRD analysis of wheat straw char between 1000 and 1500°C showed a wide range of inorganic components, mostly present as oxides (SiO_2, CaO, MgO)

^{29}Si solid-state NMR analysis

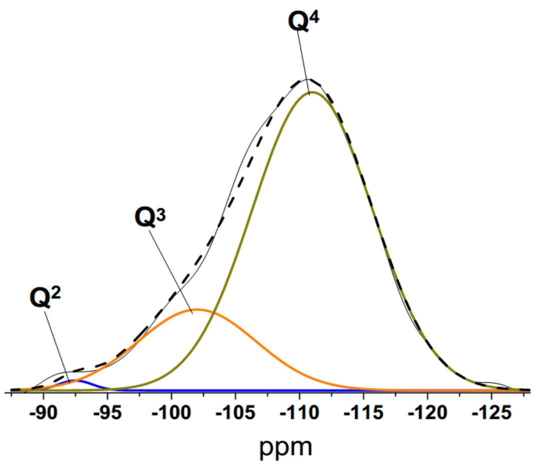
^{29}Si CP/MAS and SP/MAS NMR spectra



Original rice husk



Char, 1500°C



Q^{4*}, $[Si(OSi)_4]$: -111±3 Q^{3*}, $[(OH)Si(OSi)_3]$: -102±3 Q^{2*}, $[(OH)_2Si(OSi)_2]$: -92±5

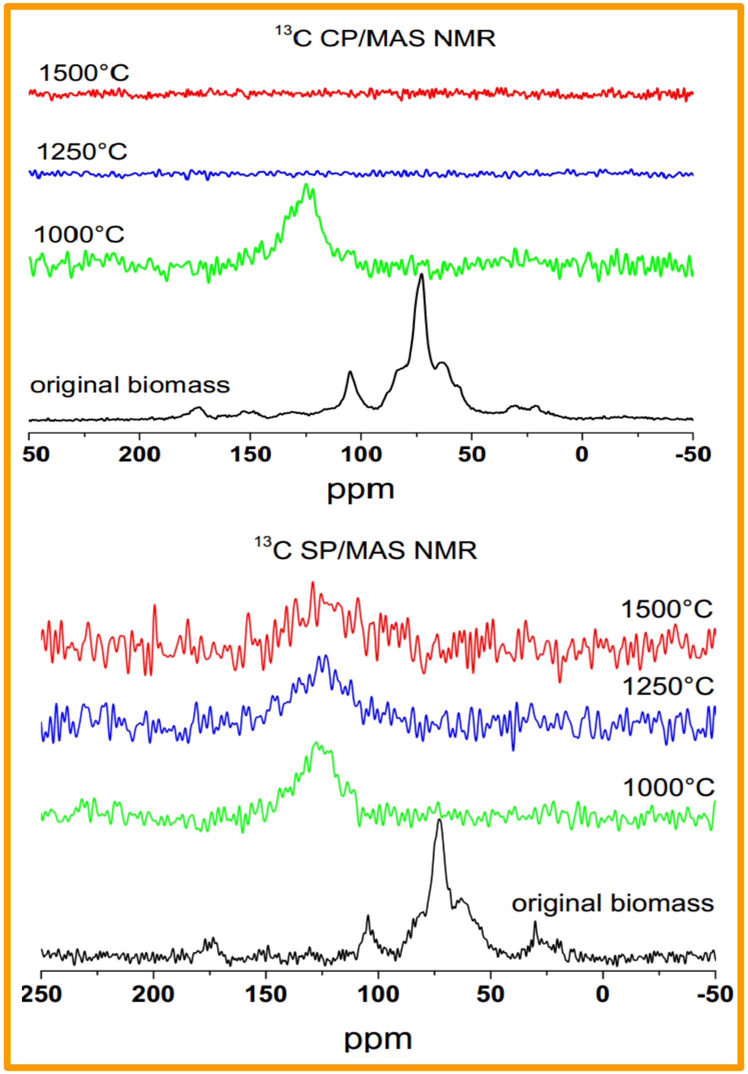
* - index of Q^4, Q^3 and Q^2 indicates the number of siloxane bonds

- The silicon oxides were most likely present in the amorphous form due to the width of the resonances originating from the Q^4 sites
- No crystalline silicon compounds were observed
- No significant changes appeared in the ^{29}Si NMR spectra and thereby in the rice husk silicate structure with the increasing temperature
- The shape of the rice husk chars remained preserved even at a higher temperature, due to the low softening temperature of amorphous silicon oxides (≈730°C)*

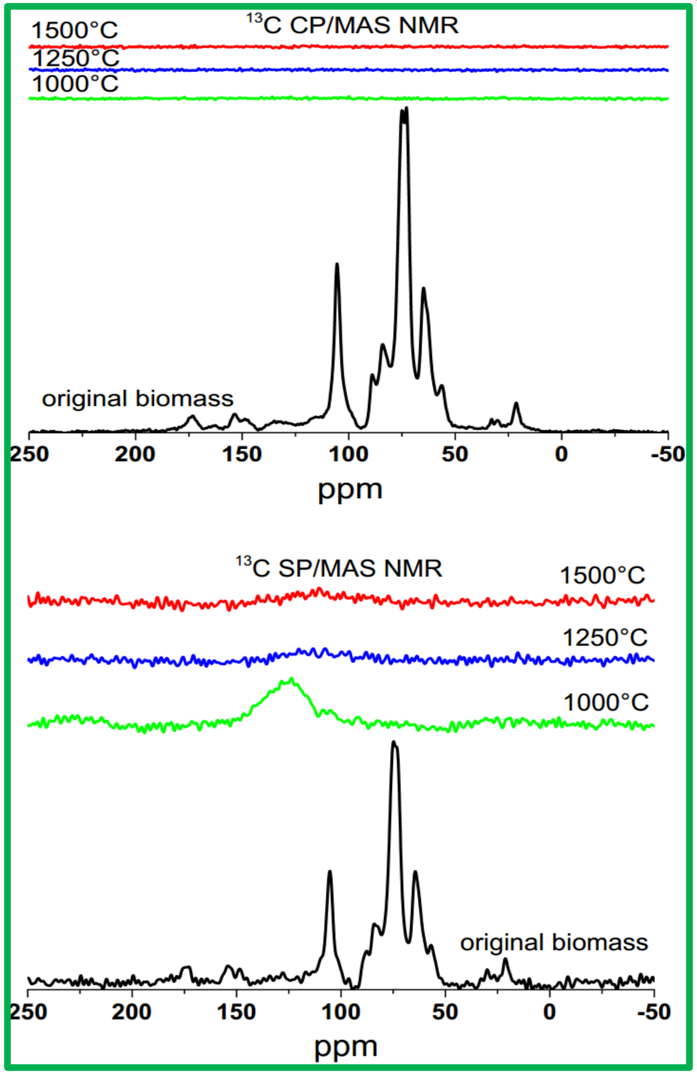
Hedler et al. 2004

^{13}C solid-state NMR analysis

Rice husk and chars



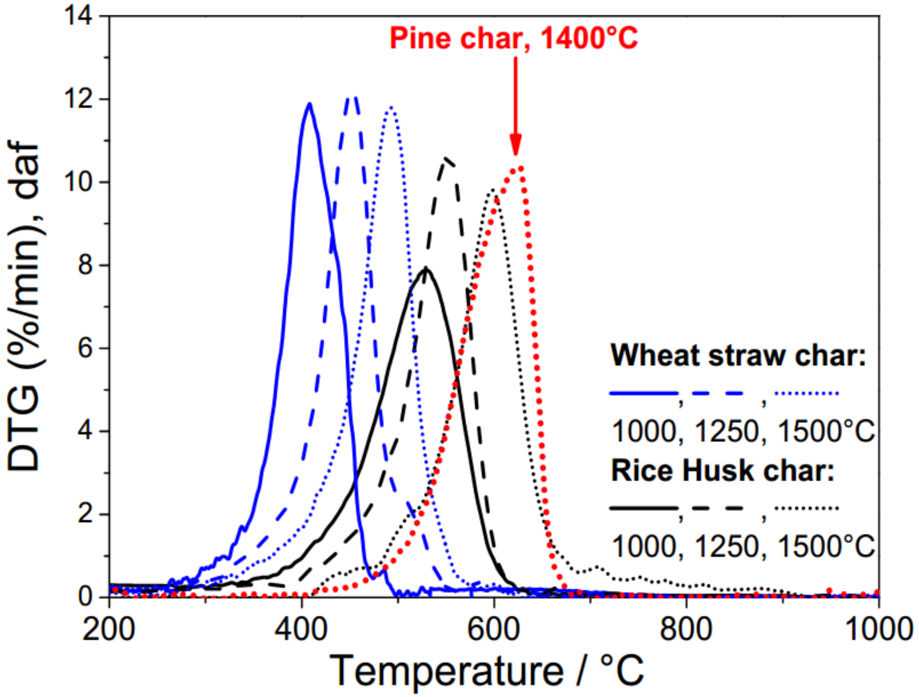
Original wheat straw and chars



- No ^{29}Si CP/MAS NMR spectra of original wheat straw and its chars were observed compared to rice husk

Silicon oxides effect on char reactivity

TGA, 5 vol.% O_2 + 95 vol. % N_2



- Reactivities of pinewood and rice husk chars were similar in oxidation, indicating less influence of silica on the char reactivity

- The alkali rich wheat straw chars were 6, 18 and 50 times more reactive than wood and rice husk chars

- The reactivity of wheat straw and rice husk chars decreased at high heat treatment temperatures due to annealing of the carbon and loss of catalytically active potassium in the case of straw

Summary

- The results of the ^{29}Si solid-state NMR study indicated that the silicates in rice husk chars were mainly amorphous
- No significant changes appeared in the ^{29}Si solid-state NMR for Q^2, Q^3 and Q^4 branches of rice husk chars
- The presence of silicates in the rice husk affected the obtained char morphology by the formation of a glassy char shell due to the softening of the amorphous silicon oxides
- Silicates present in rice husk chars did not affect the reactivity in oxidation
- High alkali content in wheat straw increased the char reactivity

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